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Analysis of Stark Spectroscopy Data

If we were organisms so sensitive that a single atom, or even a few atoms, could make a perceptible impression on our senses — Heavens, what would life be like!

— Erwin Schrödinger

What is Life?

Abstract

Stark effect spectroscopy yields the difference between the absorption spectrum of a sample in the presence of an externally applied electric field and the spectrum without the field. These difference spectra can be analyzed to yield the field dependence of excited state energy levels and transition dipoles. An essential component of this analysis is knowledge of the electric field at the sample; while there is no good solution for this problem at present, this chapter presents an improved version of the Lorentz model based on simple dielectrics. Equations for difference spectra are derived from Stark parameters (the molecular difference dipole, difference polarizability, and transition polarizability) using clearly defined assumptions, which demonstrate that difference spectra are convolutions of the corresponding absorption spectrum and a function which depends only on the Stark parameters. Due to the convolution relationship, Stark spectra are fit with the derivatives of the absorption spectrum. Inverting the equations for the Stark spectra yields the Stark parameters in terms of spectral observables. Two sets of equations are given: a set for a quick analysis of Stark effect data which assumes a simple polarization angle dependence and a set that allows a complete analysis of the Stark parameters.

Introduction

Stark effect spectroscopy measures the spectral change caused by the application of an external electric field to a sample¹. Electronic Stark spectroscopy examines the effect of a field on electronic transitions in small molecules, proteins, or other systems, yielding information on the difference in dipole moments and polarizabilities between the ground and excited states¹. Vibrational Stark spectroscopy is a newer method²⁻⁴ which has been used to study internal electric fields⁵, bond anharmonicities, and perturbations of electron clouds in molecules by electric fields^{6,7}. While relatively simple experimentally, Stark spectroscopy methods provide unique observations of the structures and electronic behaviors of molecules and proteins.

At its simplest level, Stark effect data are no more than empirically measured difference spectra; a Stark spectrum is the difference between the sample absorption with the electric field turned on and the absorption with the field turned off. These spectra need to be fit with an appropriate model function and then interpreted to yield useful information about the sample, which is the topic of this chapter. A small fraction of the results presented here has been published before in journal articles^{1,8-10}, other portions are briefly described in other doctoral dissertations¹¹⁻¹³, and much is original work. Unfortunately, few of the results are readily available in the literature, despite their utility for analysis of Stark effects. While higher order Stark spectroscopy is discussed below, it is only considered for conventional Stark effects, not for the resonant Stark effects where the technique is most useful^{14,15}.

This chapter is divided into three sections, which are largely independent of each other. (i) The first section addresses the independent variable of Stark spectroscopy, which is the electric field. Determining the actual value of an externally applied electric field at a sample molecule is surprisingly difficult since sample molecules are small enough that local electrostatic perturbations arising from the solvent or other local structure cannot be ignored. (ii) Assuming an adequate understanding of the local field can be achieved, it is possible to predict a Stark effect spectrum from molecular parameters, as shown in the second section. This calculation is rarely useful on its own but it serves to present the approximations that are typically made and it presents a qualitative understanding of the origins of Stark spectral lineshapes. (iii) Inverting the equations in the previous section, the molecular Stark effect parameters are calculated from Stark spectra. This section is likely to be the most useful one for the reader, because it presents simple equations for a quick analysis of Stark effect data, as well as the more detailed equations required for a complete analysis.

I. The Local Field

The local electric field is the field at the location of a chromophore, ignoring the field contribution created by the chromophore. Stated in a different way, it is the total field incident on the chromophore by all external sources. In the general case, the local

field is a function of the position within the chromophore volume. Also, it differs between sample molecules due to inhomogeneous solvent structure.

The local field at any point in space can be approximated as the sum of the matrix field and a term which is proportional to the external field,

$$\mathbf{F}_{\text{int}} = \mathbf{F}_{\text{matrix}} + f \cdot \mathbf{F}_{\text{ext}}. \quad (1)$$

The matrix field, $\mathbf{F}_{\text{matrix}}$, is the local field in the absence of an applied field; it accounts for the solvent reaction field¹⁶⁻¹⁹ and for the field due to other organized local structure, such as nearby protein residues²⁰⁻²². \mathbf{F}_{ext} is the average field external to the sample molecule in the nearby solvent. For the bulk measurements considered here, the external field is simply equal to the applied field, which is the applied voltage divided by the electrode spacing. The local field correction factor, f , is a tensor in a general treatment, but is typically approximated by a scalar for Stark spectroscopy¹. Also, the inhomogeneity of f within the volume of a chromophore and the variability of f between different chromophore molecules are typically ignored. While these are major approximations, they are partially justified in the following discussion of dielectrics. The local field correction factor is also a function of the electric field frequency. Only the zero frequency value is of interest for Stark effect spectroscopy but other frequencies are required by researchers interested in absolute linear²³ and non-linear²⁴ optical properties.

It is sometimes possible to largely side-step the local field issue, by reporting results in terms f . For example, linear Stark effects can be given in units of Debye/ f and quadratic Stark effects in units of $\text{\AA}^3/f^2$. This is useful for comparison of results between samples dissolved in similar solvents, because f , while unknown, is expected to remain nearly constant. Local field correction values between 1.1 and 1.4 are typically assumed for condensed phase samples^{1,24}.

The standard method for estimating the value of f assumes that the solvent behaves as a uniform linear dielectric with dielectric constant ϵ even in the inner-most solvation shell. The Lorentz spherical cavity model ignores the field due to the chromophore by considering a hypothetical system in which the chromophore is removed from the solvent, leaving a cavity²⁵. After dielectric equilibration, the field in a spherical cavity²⁶

is found to be uniform and directly proportional to the external field, with a field correction factor of

$$f = \frac{3\epsilon}{2\epsilon + 1} \quad (2)$$

It has been shown that cavities with irregular surfaces, as they must be for real molecules, lead to very similar results²⁷. While this model is commonly used, it ignores the effect of electrical polarization of the chromophore on the surrounding solvent. A preferable method is to model a chromophore in a solvent as a spherical dielectric with dielectric constant ϵ_2 , surrounded by solvent with dielectric constant ϵ_1 . With this improved model, the local field is still uniform and parallel to the external field, and the local field correction factor is

$$f = \frac{\epsilon_1(\epsilon_2 + 2)}{2\epsilon_1 + \epsilon_2} \quad (3)$$

(Derivation method: the solvent electric field is presented for a two dielectric system by Böttcher²⁶, from which the solvent polarization and solvent surface charge are calculated; keeping the solvent polarization fixed, the solute is replaced by a cavity, and the field is calculated in the cavity using the solvent surface charge.) Eq. 3 can be simplified to the spherical cavity model by assigning a value of 1 to ϵ_1 , simplifying the result to match eq. 2.

A commonly used glass-forming solvent is 2-methyl-tetrahydrofuran (2-MeTHF), which has a liquid phase room temperature dielectric constant of 6.8²⁸. Assuming that the sample has a similar dielectric constant, the local field correction value is found to be either 1.4 or 2.9, using eqs. 2 and 3, respectively. Clearly, the choice of the model makes a significant difference. However, modern Stark effect measurements are typically carried out on immobilized samples, in which both the sample and solvent dielectric constants are greatly reduced due to the lack of rotational mobility. Frozen solvent dielectric constants are rarely reported²⁹, but are straightforward to measure. By measuring the capacitance increase of a Stark effect cell between an empty cell and one filled with frozen solvent using a commercial pulsed capacitance meter, it was found that the dielectric constant for frozen 2-MeTHF is about 2.2 and that it is about 2.5 for a

frozen glycerol/water mixture. Using the frozen 2-MeTHF dielectric constant, the Lorentz model gives $f=1.2$ for 2-MeTHF, while eq. 3 gives $f=1.4$. These values are close to the ones that are typically assumed.

Rather than estimating local field correction factors from equations that assume uniform dielectrics, a preferable method may be through comparison of condensed phase Stark effect results with either vapor phase Stark results³⁰⁻³² or with high level *ab initio* calculations of either Stark effects³³ or local electric fields^{21,34}.

II. Derivation of Stark Fitting Coefficients from Stark Parameters

The basic equations of Stark spectroscopy express the shift of the transition frequency, $\omega(\mathbf{F})$, and transition dipole, $\mathbf{M}(\mathbf{F})$, as Taylor expansions in terms of the local electric field, \mathbf{F} :

$$\omega(\mathbf{F}) = \omega_0 + \frac{1}{hc} \Delta\mu \cdot \mathbf{F} + \frac{\mathbf{F} \cdot \Delta\alpha \cdot \mathbf{F}}{2} + \frac{\Delta\beta : \mathbf{F}^3}{6} + \dots \quad (4)$$

$$\mathbf{M}(\mathbf{F}) = \mathbf{M} + \mathbf{A} \cdot \mathbf{F} + \mathbf{F} \cdot \mathbf{B} \cdot \mathbf{F} + \dots \quad (5)$$

h is Planck's constant and c is the speed of light. Implicit in these expansions is the assumption that field effects are small, so effects that are higher order in the electric field may be ignored. $\Delta\mu$ is a vector called variously the difference dipole moment, the linear Stark effect, or the Stark tuning rate, and is typically the dominant factor for field dependent spectral changes. $\Delta\alpha$ is a matrix called either the difference polarizability or the quadratic Stark effect, and is typically most important for inversion symmetric systems, for which $\Delta\mu$ vanishes by symmetry; $\Delta\beta$ is the difference hyperpolarizability and is typically very small. In all cases, the differences refer to the difference between the ground state and the excited state, although this literal interpretation is misleading for vibrational transitions^{6,35}. \mathbf{A} and \mathbf{B} (capital alpha and capital beta) are the transition polarizability and transition hyperpolarizability tensors, respectively, and give rise to field dependent absorption intensity changes.

Fundamental assumptions. From Fermi's Golden Rule, the molar decadic extinction coefficient of a single molecule is given by³⁶

$$\alpha(\omega) = \frac{N_A \epsilon_0}{\epsilon_0 h \ln 10} (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \rho(\omega) \quad (6)$$

N_A is Avagadro's number, ϵ_0 is the electrical permittivity of vacuum, ω is the light frequency in wavenumbers, $\hat{\mathbf{e}}$ is a unit vector in the direction of the light polarization, \mathbf{M} is the transition dipole moment, and $\rho(\omega)$ is the density of states. The density of states term includes all effects of lifetime broadening and other homogeneous broadening, and is thus the homogeneous lineshape function. To include heterogeneous broadening, $\rho(\omega)$ is replaced by the heterogeneous lineshape function, $S(\omega)$. If one makes the assumption (#1) that different sample molecules do not interact, then the extinction coefficient of a bulk sample is simply the average of extinction coefficients for individual molecules, with proper weighting to account for the different orientations. Assuming (#2) that heterogeneous broadening is independent of orientation (this would not be the case for a crystalline matrix, for example), the bulk extinction coefficient becomes

$$\alpha(\omega) = \frac{N_A \epsilon_0}{\epsilon_0 h \ln 10} \langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \rangle S(\omega) \quad (7)$$

where the notation $\langle \dots \rangle$ indicates orientational averaging. Orientational averaging is discussed in Appendix A.

When an external electric field is applied to a sample, many things could happen. These include Stark type perturbations of energy levels, re-orientation of sample molecules, bond strength changes, chemical alterations, or even ionization. Most of these changes fundamentally, and sometimes irreversibly, change the absorption spectrum. However, we will assume that the only change that occurs is a small and reversible perturbation of the eigenstates. More precisely, we assume (#3) that the excited state lifetime and dynamics are unaffected, leading to a conserved homogeneous lineshape function¹⁵, (#4) that the heterogeneous broadening is unaffected, and (#5) that the distribution of sample molecule orientations is unaffected. The assumption of conserved heterogeneous broadening is more significant than it might appear. A primary cause of heterogeneous broadening is expected to be heterogeneity in the solvent reaction field, as discussed above, causing a range of solvent induced Stark shifts. If the molecule exhibits a significant quadratic Stark effect, then two molecules with the same orientation but

different matrix electric fields would exhibit different spectral shifts in an externally applied electric field. In this case, the bandshape would not be conserved.

In an electric field, the extinction coefficient is the same as in eq. 7, but now with a field dependent transition dipole and a transition frequency shift,

$$\epsilon_F(\nu) = \frac{N_A \nu}{c_0 h \ln 10} \left\langle [\hat{\mathbf{e}} \cdot \mathbf{M}(\mathbf{F})]^2 S(\nu \pm \nu(\nu)) \right\rangle \quad (8)$$

As before, $\nu(\nu)$ is a function of the field, although it isn't shown explicitly here, or below, for clarity. The functions $f(\nu)$ and $g(\nu)$ are defined as the field-off and field-on extinction coefficients given in eqs. 7 and 8, but without the factor of ν and the collection of constants that are the same for both equations,

$$f(\nu) \equiv \left\langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \right\rangle S(\nu) \quad (9)$$

$$g(\nu) \equiv \left\langle [\hat{\mathbf{e}} \cdot \mathbf{M}(\mathbf{F})]^2 S(\nu \pm \nu(\nu)) \right\rangle \quad (10)$$

With a couple manipulations of eqs. 9 and 10, $g(\nu)$ may be rewritten as a convolution of $f(\nu)$ with some new function, which we will call the shift function and write as $h(y)$,

$$g(\nu) = \frac{\int_y [\hat{\mathbf{e}} \cdot \mathbf{M}(\mathbf{F})]^2 f(\nu \pm y) \nu(\nu \pm y) dy}{\left\langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \right\rangle} \quad (11)$$

$$= \int_y h(y) f(\nu \pm y) dy \quad (12a)$$

$$= (f \otimes h)(\nu) \quad (12b)$$

where

$$h(y) \equiv \frac{\left\langle [\hat{\mathbf{e}} \cdot \mathbf{M}(\mathbf{F})]^2 \nu(\nu \pm y) \right\rangle}{\left\langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \right\rangle} \quad (13)$$

Thus, a function containing the entire Stark effect, $h(y)$, has been separated from the spectral lineshape. Molecules with the same Stark parameters have the same shift function, regardless of their spectra. In principle, $h(y)$ can be measured directly as the

deconvolution of a Stark spectrum with the absorption spectrum, although this is virtually never possible in practice due to signal-to-noise issues.

In the limit of zero field, $g(\Delta)$ is equal to $f(\Delta)$ and $h(y)$ is a delta function at $y=0$ with unit area (the convolution identity function). As the field is increased, $g(\Delta)$ and $h(y)$ typically become broadened and shifted, with the shape of $h(y)$ describing the difference between $f(\Delta)$ and $g(\Delta)$.

The shift function also depends on the angle between the light polarization and the applied field, which is given as θ . If the sample is isotropic, $h(y)$ is simply related to the shift functions for the limiting cases of light polarization parallel and perpendicular to the electric field, $h_{\parallel}(y)$ and $h_{\perp}(y)$, respectively,

$$h(y) = h_{\parallel}(y)\cos^2\theta + h_{\perp}(y)\sin^2\theta \quad (14)$$

This relation is found from eq. 13 or from the discussion of orientational averaging, presented in Appendix A. Rather than separating $h(y)$ into parallel and perpendicular functions, it can be separated into a θ independent term and a θ dependent term, also presented in Appendix A.

If the sample is not isotropic³⁷, then a cross-term is required as well, $h_{\times}(y)$. For convenience the field is taken to be along the Z -axis and the polarization of light is taken to be in the X - Z plane (capital letters are used for the lab frame axes and \mathbf{X} and \mathbf{Z} are unit vectors along the respective axes).

$$h_{\times}(y) = \frac{\langle [\mathbf{X} \cdot \mathbf{M}(\mathbf{F})][\mathbf{Z} \cdot \mathbf{M}(\mathbf{F})] \Delta(\Delta \Delta \Delta y) \rangle}{\langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \rangle} \quad (15)$$

$$h(y) = h_{\parallel}(y)\cos^2\theta + 2h_{\times}(y)\sin\theta\cos\theta + h_{\perp}(y)\sin^2\theta \quad (16)$$

The shift function. Before moving on to Stark effects for general situations, the shift function is considered for a couple very simple systems to illustrate the basic connections between the Stark parameters and the shift function. In all of these, sample isotropy is assumed.

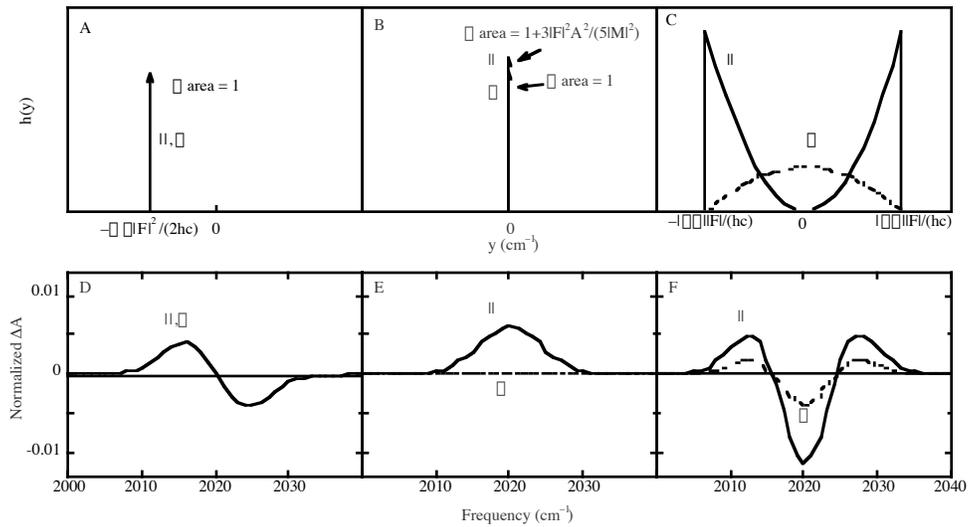


Figure 1. Components of observed Stark effects for examples described in text. (A) $\Delta \square$ is isotropic and non-zero. (B) \mathbf{A} is only non-zero for zz element. (C) $\Delta \square$ is non-zero and parallel to \mathbf{M} . In panels A and C, the abscissa typically extends over much less than 1 cm^{-1} . Panels D, E, and F show calculated Stark effects for a Gaussian peak centered at 2020 cm^{-1} with 10 cm^{-1} full width at half maximum and peak absorption of 1, in a 1 MV/cm field, using the same assumptions as panels A, B, and C. (D) $\Delta \square$ is 1 \AA^3 for each diagonal component. (E) $\mathbf{A} \cdot \mathbf{F}$ is 0.1 times \mathbf{M} . (F) $\Delta \square$ is 0.05 D . The \parallel and \square designations refer to the angle between the electric field and the light polarization.

For the first system, consider one which, by symmetry or coincidence, has most terms vanish in eqs. 1 and 2, leaving only a difference polarizability term. It is also assumed that the $\square \square$ matrix is diagonal with each diagonal term equal to the scalar $\square \square$. An example is the forbidden $1s \square 2s$ transition in the hydrogen atom (ignoring the nearly degenerate $2p$ level). The shift function in eq. 13 simplifies to just a delta function, because the delta function is independent of orientation, allowing it to be pulled out of the orientational average.

$$h(y) = \square \square y + \frac{\square \square |F|^2 \square}{2hc \square} \quad (17)$$

In this example, the absorption band of each molecule shifts the same amount, regardless of the molecule's orientation. As a result, the spectrum simply shifts to lower energy by $-\frac{1}{2}|\mathbf{F}|^2/(2hc)$. The shift function for this simple quadratic Stark effect is shown in Figure 1A.

The second system is one which exhibits only a transition polarizability, and no Stark shift. Also, the transition polarizability matrix, \mathbf{A} , is defined to have only one non-zero element, the A_{zz} component, which is set to the scalar A . This implies that a field along the molecule's z -axis modifies the magnitude of the transition dipole, while fields along other axes have no effects on the spectrum. Using the orientational averaging method discussed in Appendix A, the denominator of $h(y)$ is easily solved,

$$\langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \rangle = \frac{|\mathbf{M}|^2}{3} \quad (18)$$

The numerator is solved separately for the parallel and perpendicular shift functions, again with orientational averaging methods,

$$h_{\parallel}(y) = \frac{1}{3} + \frac{3|\mathbf{F}|^2 A^2}{5|\mathbf{M}|^2} \frac{1}{3} \Delta(y) \quad (19a)$$

$$h_{\perp}(y) = \Delta(y) \quad (19b)$$

Thus, the transition polarizability only affects the spectrum when the light polarization is at least partially parallel to the field, and the effect is maximized when they are completely parallel (figure 1B). The effect, which is simply an increase of absorption intensity, is generally quite small because it is proportional to A^2 . For example, even if a molecule's absorption increases by 10% when it is oriented parallel to an electric field, the absorption of an isotropic sample only increases by less than 1%.

As a final example, suppose that only the difference dipole is significant and that it is parallel to the transition dipole moment. This system is the one most similar to typical systems studied experimentally. The denominator of $h(y)$ is the same as in the previous example, given in eq. 18. However, the numerator takes more work to solve, and, because the delta function does not pull out of the average, standard orientational averaging methods are of minimal use. Instead, the averaging integral has to be done

explicitly. The only important Euler angle here is θ , which is defined as the angle between \mathbf{M} and the Z axis. Solving first for $h_{\parallel}(y)$,

$$\begin{aligned}
 h_{\parallel}(y) &= \frac{3}{|\mathbf{M}|^2} \left\langle (\mathbf{Z} \cdot \mathbf{M})^2 \frac{|\mathbf{F}| \cos \theta}{hc} y \right\rangle \\
 &= \frac{3}{|\mathbf{M}|^2} \left\langle |\mathbf{M}|^2 \cos^2 \theta \frac{|\mathbf{F}| \cos \theta}{hc} y \right\rangle \\
 &= \frac{3}{2} \int_0^{\pi} \cos^2 \theta \frac{|\mathbf{F}| \cos \theta}{hc} y \sin \theta d\theta \\
 &= \frac{3}{2} \int_1^{-1} \cos^2 \theta \frac{|\mathbf{F}| \cos \theta}{hc} y d(\cos \theta) \\
 &= \begin{cases} \frac{3y^2}{2} \frac{hc}{|\mathbf{F}|} & \text{for } |y| < \frac{|\mathbf{F}|}{hc} \\ 0 & \text{for } |y| > \frac{|\mathbf{F}|}{hc} \end{cases} \tag{20a}
 \end{aligned}$$

The derivation of $h_{\perp}(y)$ is very similar. The differences are that $(\hat{\mathbf{e}} \cdot \mathbf{M})^2$ becomes $|\mathbf{M}|^2 \cos^2 \theta \sin^2 \theta$, and there is an integral over all θ as well. The result is

$$\begin{aligned}
 h_{\perp}(y) &= \begin{cases} \frac{3hc}{4|\mathbf{F}|} \frac{hcy^2}{|\mathbf{F}|} & \text{for } |y| < \frac{|\mathbf{F}|}{hc} \\ 0 & \text{for } |y| > \frac{|\mathbf{F}|}{hc} \end{cases} \tag{20b}
 \end{aligned}$$

These shift functions are shown in Figure 1C. To interpret the functions, it is seen that the band shift of a molecule oriented parallel to the field is $\Delta E_{\parallel} = |\mathbf{F}|/hc$, and the shift is less for other angles. Due to sample isotropy, half the molecules have spectra that shift to lower energy, while the other half shift to higher energy, leading to a symmetric $h(y)$ and to a net band broadening. Meanwhile, the molecules that are detected best are those oriented with their transition dipoles parallel to the light polarization, leading to the differences between $h_{\parallel}(y)$ and $h_{\perp}(y)$.

Moments of the shift function. While the shift function is nice conceptually, it is nearly impossible to measure it accurately and it is nearly impossible to derive it for all

but the simplest cases. The solution is to expand the shift function in terms of its moments, which is done using a couple Fourier transform identities. The notation used here is that $a(\bar{\nu})$ or $a(y)$ is a function in wavenumber space, while $\hat{a}(x)$ is its Fourier transform in position space. Starting with eq. 12,

$$\begin{aligned}
 g(\bar{\nu}) &= (f \otimes h)(\bar{\nu}) && \text{definition of convolution} \\
 \hat{g}(x) &= \sqrt{2\pi} \hat{f}(x) \hat{h}(x) && \text{convolution theorem} \\
 &= \sqrt{2\pi} \hat{f}(x) \sum_j \frac{1}{j!} \hat{h}^{(j)}(0) x^j && \text{Taylor expansion of } \hat{h}(x) \\
 &= \sqrt{2\pi} \sum_j \frac{i^j}{j!} \widehat{f^{(j)}}(x) \hat{h}^{(j)}(0) && \text{derivative theorem} \\
 g(\bar{\nu}) &= \sqrt{2\pi} \sum_j \frac{i^j}{j!} \hat{h}^{(j)}(0) f^{(j)}(\bar{\nu}) && \text{inverse transform} \quad (21)
 \end{aligned}$$

Thus, $g(\bar{\nu})$ is expanded in terms of the derivatives of $f(\bar{\nu})$. The expansion coefficients may be simplified some.

$$\begin{aligned}
 \hat{h}^{(j)}(x) &= \left[(\pi i y)^j \widehat{h(y)} \right] (x) && \text{derivative theorem} \\
 \hat{h}^{(j)}(0) &= \frac{i^j}{\sqrt{2\pi}} \int_y y^j h(y) dy && \text{inverse transform at } x=0 \\
 &= \frac{i^j}{\sqrt{2\pi}} m_j \quad \text{where} \quad m_j \equiv \int_y y^j h(y) dy && \text{definition of } m_j \quad (22)
 \end{aligned}$$

The m_j terms are the moments of $h(y)$. Finally,

$$\begin{aligned}
 g(\bar{\nu}) &= \sum_j \frac{(\pi i)^j m_j}{j!} f^{(j)}(\bar{\nu}) \\
 &= m_0 f(\bar{\nu}) + m_1 f'(\bar{\nu}) + \frac{m_2}{2} f''(\bar{\nu}) + \frac{m_3}{3!} f'''(\bar{\nu}) + \dots \quad (23)
 \end{aligned}$$

This gives the Stark spectrum as a sum of derivatives of the absorption spectrum, where the coefficients are the moments of the shift function. The expansion coefficients are measurable variables, as explained below. There are several interpretations for the m_j

terms. They are the moments of $h(y)$, or, essentially, the Taylor expansion coefficients of $\hat{h}(x)$. Another view is that the function $h(y)$ is zero except across a narrow region near the origin (Fig. 1). Due to its finite extent, it may be expanded as a delta function, plus the first, second, and higher order derivatives of the delta function; the m_j terms are the expansion coefficients for this sum of delta function derivatives. Regardless of the interpretation, the important point is that any convolution can be rewritten as a sum of the derivatives of one of the functions; similarly a sum of derivatives can be rewritten as a convolution.

Stark spectral lineshapes. Since a Stark spectrum can be expressed as a convolution and a convolution can be expressed as a sum of derivatives of one of the functions, Stark spectra are fit with the derivatives of the absorption spectrum. Due to the factors of ν in eqs. 7 and 8, spectra can be divided by ν before fitting to yield

$$g(\nu) \propto f(\nu) = Z_0 f(\nu) + Z_1 f'(\nu) + Z_2 f''(\nu) + \dots \quad (24a)$$

Z_0 is called the zeroth derivative contribution, Z_1 is the first derivative contribution, and so on. An equivalent expression yields a fit of the Stark difference spectrum in terms of frequency weighted derivatives of the absorption spectrum,

$$\nu f(\nu) = Z_0 \nu f(\nu) + Z_1 \nu \frac{\partial}{\partial \nu} \frac{\nu f(\nu)}{\nu} + Z_2 \nu \frac{\partial^2}{\partial \nu^2} \frac{\nu f(\nu)}{\nu} + \dots \quad (24b)$$

The m_j coefficients are closely related to both these fit coefficients and to the commonly published parameters, A_ν , B_ν , and C_ν (although the latter ones are just the coefficients for Stark effects that are proportional to $|\mathbf{F}|^2$, whereas the m_j coefficients include higher order field contributions as well).

$$m_0 = Z_0 + 1 = A_\nu |\mathbf{F}|^2 + 1 \quad (25)$$

$$m_1 = \nu Z_1 = \nu \frac{B_\nu |\mathbf{F}|^2}{15hc} \quad (26)$$

$$m_2 = 2Z_2 = \frac{C_\nu |\mathbf{F}|^2}{15h^2c^2} \quad (27)$$

Returning to the definition of $h(y)$ in eq. 13, the m_j coefficients are derived from the Stark parameters,

$$m_j = \frac{1}{\langle (\hat{\mathbf{e}} \cdot \mathbf{M})^2 \rangle_y} \int y^j \langle [\hat{\mathbf{e}} \cdot \mathbf{M}(\mathbf{F})]^2 \Delta(\Delta y) \rangle dy$$

$$= \frac{3}{|\mathbf{M}|^2} \langle [\hat{\mathbf{e}} \cdot \mathbf{M}(\mathbf{F})]^2 (\Delta y)^j \rangle \quad (28)$$

This final equation forms a link between the molecular Stark parameters and the measurable fit coefficients. At this point, it is straightforward, though lengthy, to derive the m_j values for the general case, which is done below. First, though, it is instructive to return to the three examples for which $h(y)$ was solved exactly.

For the first example, in which only Δy is non-zero,

$$m_{j\parallel} = m_{j\perp} = \frac{\langle \Delta y^j |\mathbf{F}|^2 \rangle}{2hc} \quad (29)$$

Electronic Stark spectroscopy is typically measured with a lock-in amplifier, tuned to the n 'th harmonic of the field frequency, yielding an n 'th Stark spectrum. An n 'th Stark measurement selects only the terms of the Stark difference spectrum that are proportional to $|\mathbf{F}|^n$. Thus, in this example a 2nd Stark measurement will show a first derivative lineshape (m_1 is non-zero), a 4th measurement shows a second derivative lineshape (m_2 is non-zero), 6th is exclusively third derivative, and so forth. A DC Stark effect measurement measures all field components at once, so a DC Stark spectrum for this example system has all derivative contributions, except the zeroth. Since experimental fields are small though, the $|\mathbf{F}|^2$ term dominates and the result is essentially a first derivative lineshape, as seen in Figure 1D.

For the second example, with only \mathbf{A} , only the m_0 term is non-zero which leads to what's called a zeroth derivative lineshape (Figure 1E),

$$m_{0\parallel} = 1 + \frac{3A^2 |\mathbf{F}|^2}{5|\mathbf{M}|^2}$$

$$m_{0\perp} = 1 \quad (30)$$

Here, only the 2^{nd} Stark spectrum is affected, and the result only appears in the zeroth derivative contribution.

Finally, in the third example, with only $\Delta\alpha$, the odd j terms are zero, while the even ones are given by

$$m_{j\parallel} = \frac{3}{j+3} \frac{\langle \Delta\alpha \rangle \langle \mathbf{F} \rangle^j}{hc}$$

$$m_{j\perp} = \frac{3}{(j+1)(j+3)} \frac{\langle \Delta\alpha \rangle \langle \mathbf{F} \rangle^j}{hc} \quad (31)$$

A 2^{nd} Stark spectrum is only second derivative, 4^{th} is only fourth derivative, and so forth. As before, a DC Stark spectrum has all these components, but the $|\mathbf{F}|^2$ term dominates, seen by the second derivative lineshape in Figure 1F.

When multiple Stark parameters are combined, such as \mathbf{A} and $\Delta\alpha$, cross-terms are created that yield more complex Stark spectra and other derivative contributions than just those listed for these simple cases. Nevertheless, for either standard 2^{nd} Stark spectroscopy or DC Stark spectroscopy, zeroth derivative contributions are generally associated with the transition polarizability and second derivative contributions with the difference dipole. The first derivative contribution may result from either a difference polarizability, as is typical for electronic transitions³⁸, or from the cross-term of \mathbf{A} and $\Delta\alpha$, as is typical for vibrational transitions⁷.

General derivative coefficients. Finally, the derivative coefficients for the general case are derived, from an expansion of eq. 28,

$$m_j = \frac{3}{h^j c^j |\mathbf{M}|^2} \left\langle \left[\hat{\mathbf{e}} \cdot \mathbf{M} + \hat{\mathbf{e}} \cdot \mathbf{A} \cdot \mathbf{F} \right]^2 \Delta\alpha \cdot \mathbf{F} + \frac{1}{2} \mathbf{F} \cdot \Delta\alpha \cdot \mathbf{F} \right\rangle^j \quad (32)$$

Moments (derivative contributions) are derived for only lowest order polarizabilities and for 2^{nd} and 4^{th} Stark spectra. However, the transition hyperpolarizability is also included in the zeroth moment, because that is the only equation where its effect is seen in the 2^{nd} spectrum. If it can be assumed that the Stark parameter tensors ($\Delta\alpha$, \mathbf{A} , and \mathbf{B}) are

symmetric, which is generally not the case, the equations given below can be simplified some, as published previously^{1,13}.

$$\begin{aligned}
 m_0 = & 1 \\
 & + \frac{|\mathbf{F}|^2}{3|\mathbf{M}|^2} \left[\text{Tr} \mathbf{A}^T \mathbf{A} + 2 M_i B_{ij} \right. \\
 & \left. + \frac{3 \cos^2 \theta}{10} \left[2 \text{Tr} \mathbf{A}^T \mathbf{A} + 3(\text{Tr} \mathbf{A})^2 + 3 \text{Tr}(\mathbf{A}^2) \right] \right. \\
 & \left. + \frac{1}{15} (B_{ij} B_{ikk} + B_{ijk} B_{ijk} + B_{ijk} B_{ikj}) \right. \\
 & \left. + \frac{3 \cos^2 \theta}{70} \left[\frac{4}{3} (B_{ij} B_{ikk} + B_{ijk} B_{ijk} + B_{ijk} B_{ikj}) + (B_{ij} + B_{ji}) (B_{jkk} + B_{kkj} + B_{kjk}) \right. \right. \\
 & \left. \left. + B_{ijk} (B_{jik} + B_{kij} + B_{jki} + B_{kji}) + B_{ijj} (B_{kik} + B_{kki}) \right] \right. \\
 & \left. + O(|\mathbf{F}|^6) \right.
 \end{aligned} \tag{33}$$

$$\begin{aligned}
 m_1 = & \frac{|\mathbf{F}|^2}{hc|\mathbf{M}|^2} \left[\frac{|\mathbf{M}|^2 \text{Tr} \mathbf{A} + 2 \mathbf{M} \mathbf{A}}{6} + \frac{2 \mathbf{M} \mathbf{A}}{3} \right. \\
 & \left. + \frac{3 \cos^2 \theta}{5} \left[\frac{2 |\mathbf{M}|^2 \text{Tr} \mathbf{A} + 2 \mathbf{M} \mathbf{A}}{12} + \frac{2 \mathbf{M} \mathbf{A}}{4} + \frac{2 \mathbf{M} \mathbf{A}}{3} \right] \right. \\
 & \left. + \frac{1}{30} (\text{Tr} \mathbf{A}^T \mathbf{A} \text{Tr} \mathbf{A} + 2 \text{Tr} \mathbf{A} \mathbf{A}^T) \right. \\
 & \left. + \frac{|\mathbf{F}|^4}{hc|\mathbf{M}|^2} \left[\frac{3 \cos^2 \theta}{140} \left[\frac{4 \text{Tr} \mathbf{A}^T \mathbf{A} \text{Tr} \mathbf{A}}{3} + \frac{8 \text{Tr} \mathbf{A} \mathbf{A}^T}{3} + (\text{Tr} \mathbf{A})^2 \text{Tr} \mathbf{A} + 2 \text{Tr} \mathbf{A} \text{Tr} \mathbf{A}^T \right. \right. \right. \\
 & \left. \left. + 2 \text{Tr} \mathbf{A} \text{Tr} \mathbf{A} + \text{Tr} \mathbf{A}^2 \text{Tr} \mathbf{A} + 2 \text{Tr} \mathbf{A} \mathbf{A}^T + 2 \text{Tr} \mathbf{A} \mathbf{A} + 2 \text{Tr} \mathbf{A}^T \mathbf{A} \right] \right. \\
 & \left. + O(|\mathbf{F}|^6) \right.
 \end{aligned} \tag{34}$$

$$m_2 = \frac{|\mathbf{F}|^2 |\boldsymbol{\mu}|^2}{3h^2 c^2} + \frac{1}{5} (3\cos^2\theta - 1) (3\cos^2\theta - 1) \left[\frac{1}{60|\mathbf{M}|^2} \left(|\mathbf{M}|^2 \left((\text{Tr}\boldsymbol{\mu}\boldsymbol{\mu})^2 + \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu}^T \boldsymbol{\mu}\boldsymbol{\mu} + \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu}^2 \right) + 8\mathbf{M}\mathbf{A} \left(\boldsymbol{\mu}\boldsymbol{\mu}^T \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu}^T \boldsymbol{\mu}\boldsymbol{\mu} \right) \right) + 4\text{Tr}\mathbf{A}^T \mathbf{A} |\boldsymbol{\mu}|^2 + 8\boldsymbol{\mu}\mathbf{A}^T \mathbf{A} \boldsymbol{\mu} \right] + \frac{|\mathbf{F}|^4}{h^2 c^2} + \frac{3\cos^2\theta - 1}{420|\mathbf{M}|^2} \left[2|\mathbf{M}|^2 \left((\text{Tr}\boldsymbol{\mu}\boldsymbol{\mu})^2 + \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu}^T \boldsymbol{\mu}\boldsymbol{\mu} + \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu}^2 \right) + 3\mathbf{M} \left(2\boldsymbol{\mu}\boldsymbol{\mu}^T \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu}^T + 2\boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu}^T \boldsymbol{\mu}\boldsymbol{\mu} \right) \mathbf{M} + 4\mathbf{M} \left(4\mathbf{A} + 3\mathbf{A}^T \right) \left(\text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu}^T \right) \boldsymbol{\mu}\boldsymbol{\mu} + 12\mathbf{M}\boldsymbol{\mu}\boldsymbol{\mu} \left(\text{Tr}\mathbf{A}\text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + \text{Tr}\mathbf{A}^T \boldsymbol{\mu}\boldsymbol{\mu} + \text{Tr}\mathbf{A}\boldsymbol{\mu}\boldsymbol{\mu}^T \right) + 12\mathbf{M} \left(\boldsymbol{\mu}\boldsymbol{\mu} + \boldsymbol{\mu}\boldsymbol{\mu}^T \right) \left(\text{Tr}\mathbf{A} + \mathbf{A}^T + \mathbf{A} \right) \boldsymbol{\mu}\boldsymbol{\mu} + 2\boldsymbol{\mu}\boldsymbol{\mu} \left(4\text{Tr}\mathbf{A}^T \mathbf{A} + 8\mathbf{A}^T \mathbf{A} + 3(\text{Tr}\mathbf{A})^2 + 12\mathbf{A}\text{Tr}\mathbf{A} + 3\text{Tr}\mathbf{A}^2 + 12\mathbf{A}\mathbf{A} + 6\mathbf{A}\mathbf{A}^T \right) \boldsymbol{\mu}\boldsymbol{\mu} \right] + O(|\mathbf{F}|^6) \tag{35}$$

$$m_3 = \frac{|\mathbf{F}|^4}{h^3 c^3 |\mathbf{M}|^2} + \frac{3\cos^2\theta - 1}{140} \left[\frac{|\mathbf{M}|^2}{10} \left(|\boldsymbol{\mu}|^2 \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + 2\boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu} \right) + \frac{2}{5} \mathbf{M}\mathbf{A}\boldsymbol{\mu}\boldsymbol{\mu} \right] + \frac{4|\mathbf{M}|^2 |\boldsymbol{\mu}|^2 \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + 8|\mathbf{M}|^2 \boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu} + 6|\boldsymbol{\mu}|^2 \mathbf{M}\boldsymbol{\mu}\boldsymbol{\mu}\mathbf{M}}{140} + 2\boldsymbol{\mu}\boldsymbol{\mu} \left(3\mathbf{M}\boldsymbol{\mu}\boldsymbol{\mu}^T \text{Tr}\boldsymbol{\mu}\boldsymbol{\mu} + 6\mathbf{M}\boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu} + 6\boldsymbol{\mu}\boldsymbol{\mu}\boldsymbol{\mu}\mathbf{M} \right) + 16\mathbf{M}\mathbf{A}\boldsymbol{\mu}\boldsymbol{\mu}^2 + 12\boldsymbol{\mu}\mathbf{A}\mathbf{M}|\boldsymbol{\mu}|^2 + 3(\mathbf{M}\boldsymbol{\mu}\boldsymbol{\mu}) \left(8\boldsymbol{\mu}\mathbf{A}\boldsymbol{\mu}\boldsymbol{\mu} + 4\text{Tr}\mathbf{A}|\boldsymbol{\mu}|^2 \right) \right] + O(|\mathbf{F}|^6) \tag{36}$$

$$m_4 = \frac{|\mathbf{F}|^4 |\boldsymbol{\mu}|^4}{5h^4 c^4} + \frac{2}{7} (3\cos^2\theta - 1) (3\cos^2\theta - 1) + O(|\mathbf{F}|^6) \tag{37}$$

Several things are worth noting in these equations. First, only m_0 , m_1 , and m_2 include $|\mathbf{F}|^2$ terms, so these are the only terms that appear in a 2σ Stark spectrum and they also dominate the Stark effects with weak electric fields. The zeroth moment is associated exclusively with the transition polarizabilities. The second moment of the 2σ spectrum and the fourth moment of the 4σ spectrum are functions of only the difference dipole. 4σ spectra include order higher derivative contributions than 2σ spectra, resulting in more structured lineshapes. Finally, each equation has a term independent of θ (the magic angle term, $m_{j_{\text{ma}}}$) and a term proportional to $3\cos^2\theta - 1$ (the slope term, m_{j_s}).

III. Stark Parameters from Fitting Coefficients

From the equations above, a Stark spectrum can be calculated from a set of Stark parameters. However, it is typically more desirable to determine Stark parameters from the experimental spectrum. The first step in data analysis is to fit Stark spectra with frequency weighted derivatives of the absorption spectrum, yielding the fitting coefficients, Z_0 to Z_2 (eq. 24). Plotting these coefficients as a function of $(3\cos^2\theta-1)$ should yield a straight line if the basic assumptions in the previous section are valid⁷; the line slope and intercept are the slope and magic angle values for the fit parameters, Z_{js} and Z_{jma} ; also $Z_{j\perp}$ are the fit parameters for $\theta=90^\circ$, which are used in some equations below. The equations in this section only consider 2θ Stark effects (DC Stark effects are typically identical within noise to 2θ Stark effects, with experimentally achievable fields).

As there are only six observables in a standard 2θ Stark spectrum, which are the magic angle and slope terms of Z_0 , Z_1 , and Z_2 , and many more than six components in the Stark parameters, several assumptions have to be made. A reasonable set of assumptions on the Stark parameters is to assume that \mathbf{B} is zero and \mathbf{A} and $\Delta\theta$ are diagonal:

$$\mathbf{A} = \begin{bmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{bmatrix} \quad \Delta\theta = \begin{bmatrix} \Delta\theta_{\perp} & 0 & 0 \\ 0 & \Delta\theta_{\perp} & 0 \\ 0 & 0 & \Delta\theta_{\parallel} \end{bmatrix} \quad (38)$$

The $\Delta\theta$ approximation is valid for any system with rotational symmetry about the transition dipole moment.

Transition polarizability. With these assumptions, the following results are derived, from the zeroth derivative results (eq. 33):

$$\text{Tr}(\mathbf{A}^2) = \frac{3|\mathbf{M}|^2}{|\mathbf{F}|^2} Z_{0ma} \quad \text{and} \quad (\text{Tr}\mathbf{A})^2 = \frac{10|\mathbf{M}|^2}{|\mathbf{F}|^2} Z_{0s} \frac{\text{Tr}(\mathbf{A}^2)}{3} \quad (39)$$

These equations give two measures for \mathbf{A} , which are converted into A_{\parallel} and A_{\perp} , as follows. A pair of ratios are defined and related to each other,

$$R \equiv \frac{(\text{Tr}\mathbf{A})^2}{\text{Tr}(\mathbf{A}^2)} \quad \text{and} \quad a \equiv \frac{A_{\perp}}{A_{\parallel}} \quad (40)$$

$$a = \frac{2 \pm \sqrt{4 - 2(2 - R)(1 - R)}}{2(2 - R)} \quad (41)$$

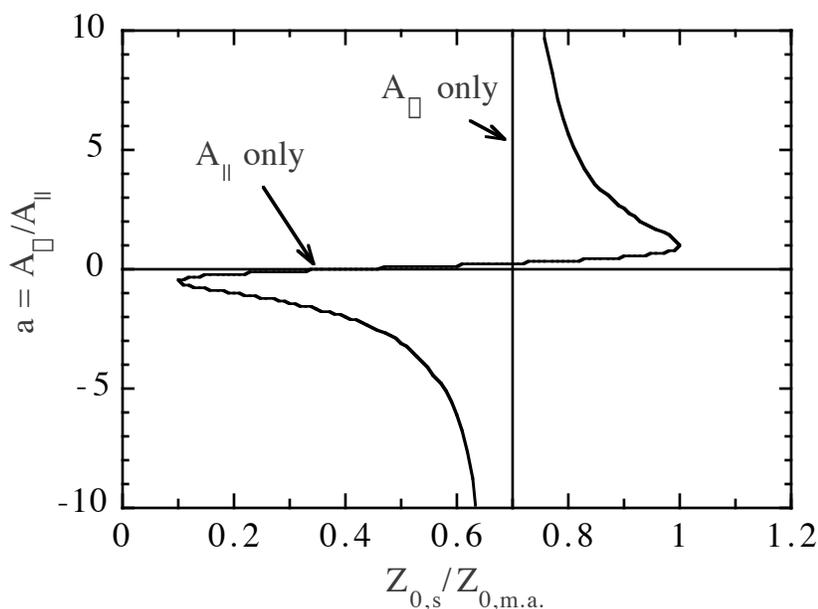


Figure 2. Solutions for transition polarizability orientation in terms of angle dependence of zeroth derivative fit coefficient. A slope ratio of 0.4 implies that A_{\perp} is 0 or that $A_{\perp} = -2A_{\parallel}$; a ratio of 0.7 implies that A_{\parallel} is 0 or that $A_{\perp} = 4A_{\parallel}$. Slope ratios cannot be less than 0.1 or greater than 1, with the assumptions stated in eq. 38 and previously in the text.

a , which can be positive or negative, is a measure of the orientation of the transition polarizability; it is small if the transition polarizability is predominantly along the transition dipole. From eq. 41, there are two possible solutions for a : a_+ and a_- . As the correct one cannot be determined from experiment, it is worth looking at these equations a little more carefully. It is found that $-0.5 < a_+ < 1$ and $-\infty < a_- < -0.5$ or $1 < a_- < \infty$. These results are shown in figure 2, using the slope to intercept ratio of the zeroth derivative fit

coefficients, which is an experimental observable, as the independent variable. If A_{\parallel} is assumed to dominate the transition polarizability, then a_+ is the correct solution. Finally, the desired parameters are found,

$$A_{\perp} = \sqrt{(\text{Tr}\mathbf{A})^2} \left| \frac{a}{2a+1} \right| \quad \text{and} \quad A_{\parallel} = \frac{A_{\perp}}{a} \quad (42)$$

Eq. 39 can also be used to show that Z_0 is a positive number at any θ angle, for all Stark effects that follow the minimal assumptions listed at the beginning of the previous section (this result turns out to be true for all transition polarizability matrices, and not just the ones assumed in eq. 38). This may be used as a fitting constraint, or as a check on the validity of the assumptions.

Difference dipole. The second derivative component is easier to interpret. From simple rearrangements of eq. 35, one gets:

$$|\Delta\alpha| = \frac{hc}{|\mathbf{F}|} \sqrt{6Z_{2ma}} \quad \text{and} \quad \cos\theta = \sqrt{\frac{5Z_{2s}}{3Z_{2ma}} + \frac{1}{3}} \quad (43)$$

As with the zeroth derivative fitting contribution, these equations show that the Z_2 is a positive number at any θ angle (again, this only depends on the approximations made in the previous section).

Difference polarizability. Finally, the first derivative can be used for $\Delta\alpha$, after subtracting the cross-terms from \mathbf{A} and $\Delta\alpha$,

$$\begin{aligned} \text{Tr}\Delta\alpha &= \frac{6hcZ_{1ma}}{|\mathbf{F}|^2} - 4 \frac{A_{\parallel}}{|\mathbf{M}|^2} |\Delta\alpha| \cos\theta \\ \Delta\alpha_{\parallel} &= \frac{10hcZ_{1s}}{|\mathbf{F}|^2} + \frac{\text{Tr}\Delta\alpha}{3} - 4 |\Delta\alpha| \cos\theta \left[\frac{2A_{\parallel}}{3|\mathbf{M}|} + \frac{A_{\perp}}{|\mathbf{M}|} \right] \\ \Delta\alpha_{\perp} &= \frac{\text{Tr}\Delta\alpha - \Delta\alpha_{\parallel}}{2} \end{aligned} \quad (44)$$

The first derivative fitting contribution, Z_1 , may be positive or negative, depending upon the values of $\Delta\alpha$, \mathbf{A} , and $\Delta\alpha$.

One dimensional system. The above equations yield the most information possible from a complete set of angle dependent set of Stark effect data. However, it is often the case that data are only collected with the light polarized perpendicular to the electric field (sample cell at normal incidence to the light beam). In this case, the best that can be done is to add further approximations, and consider Stark effects for a one dimensional system, in which $A_{\parallel}=0$, $\Delta\alpha_{\parallel}=0$, and $\alpha_{\parallel}=0$. If this assumption is valid, angle dependent fit results have slope to intercept ratios, m_{js}/m_{jma} , of exactly 0.4 for all three derivative components. In terms of the fit coefficients for $\theta=90^\circ$, the Stark parameters are:

$$A_{\parallel} = \pm \sqrt{\frac{5|\mathbf{M}|^2 Z_{0,\parallel}}{|\mathbf{F}|^2}} \quad (45)$$

$$|\alpha_{\parallel}| = \sqrt{\frac{10h^2 c^2 Z_{2,\parallel}}{|\mathbf{F}|^2}} \quad (46)$$

$$\alpha_{\parallel} = \frac{10hc}{|\mathbf{F}|^2} (Z_{1,\parallel} \pm 2\sqrt{2Z_{0,\parallel} Z_{2,\parallel}}) \quad (47)$$

For the Stark spectroscopist who is exceptionally averse to algebra, numbers can be substituted into eqs. 45 to 47 to yield the Stark parameters in their customary units. It is assumed below that the field is 1 MV/cm, that $Z_{0,\parallel}$ is unitless, $Z_{1,\parallel}$ has units of cm^{-1} , and $Z_{2,\parallel}$ has units of cm^{-2} .

$$A_{\parallel} = \pm 2.236 |\mathbf{M}| \sqrt{Z_{0,\parallel}} \quad (48)$$

$$|\alpha_{\parallel}| = 0.18832 \sqrt{Z_{2,\parallel}} \quad (49)$$

$$\alpha_{\parallel} = 178.5 Z_{1,\parallel} \pm 504.97 \sqrt{Z_{0,\parallel} Z_{2,\parallel}} \quad (50)$$

$A_{\parallel}/|\mathbf{M}|$ has units of $(\text{MV}/\text{cm})^{-1}$, $|\alpha_{\parallel}|$ is in D, and α_{\parallel} is in \AA^3 of polarizability volume.

Conclusions

Three aspects of the analysis of Stark spectroscopy are discussed here, which show the capabilities and limitations of the data.

A formula for the local field correction factor was derived which is expected to be an improvement over the standard Lorentz model. However, the values of the correction

factor are not changed significantly for frozen solvents; moreover, the improvement does not address the principal limitations of dielectric models, which is that they are only strictly accurate for volumes that are much larger than molecular dimensions. The most promising methods for determining local fields are either *ab initio* calculation of the fields^{21,34} or comparison of Stark effect measurements with independent determinations of the Stark effect (such as *ab initio* methods^{39,21}).

Starting with a set of assumptions about Stark effects, where the primary one is that the bandshape is unaffected by an electric field, the spectral response was calculated for a given set of Stark parameters. Because of these assumptions, it is possible to express a Stark lineshape as a convolution of the corresponding absorption spectrum with a separate function which depends only on the Stark parameters, called the shift function. Corollaries are that *i*) it is possible to analyze Stark spectra in terms of the derivatives of the absorption spectrum and *ii*) an entire 2π Stark spectrum can only yield up to three independent pieces of information (fit coefficients for the three derivative components). DC Stark spectra (as opposed to measurements with a lock-in amplifier) can yield more information in principle, but generally cannot do so in practice because of the low fields achievable and noise limitations. Collecting Stark spectra as a function of the θ angle doubles the possible information to six values.

Inverting the calculations of Stark spectra yields the molecular Stark parameters in terms of fitting coefficients. Eqs. 48 to 50 are useful for a basic analysis of Stark data collected with the light polarization perpendicular to the electric field. An analysis of angle dependent data is not much more difficult, using eqs. 39 to 44, and yields parallel and perpendicular components of the transition polarizability and the difference polarizability matrices, as well as the angle between the difference dipole and the transition dipole. It is found that the zeroth and second derivative fitting contributions are expected to be positive values. This may be used as a fitting constraint or to identify systems that do not obey the basic assumptions of conventional (non-resonant) Stark effects.

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